

**PCT**WORLD INTELLECTUAL PROPERTY  
ORGANIZATION  
International I

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606136A1

<b>(51) International Patent Classification 6 :</b> <b>C08L 69/00, C08K 3/34, 7/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 96/06136</b> <b>(43) International Publication Date:</b> 29 February 1996 (29.02.96)
<b>(21) International Application Number:</b> PCT/US95/09940 <b>(22) International Filing Date:</b> 4 August 1995 (04.08.95) <b>(30) Priority Data:</b> 08/294,164 22 August 1994 (22.08.94) US <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). <b>(72) Inventors:</b> LAUGHNER, Michael, K.; 1403 North Road, Lake Jackson, TX 77566 (US). MILLER, Robert, C.; 5220 Hedgewood Drive, No. 908, Midland, MI 48640 (US). <b>(74) Agent:</b> MORSE, Jonathan, W.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FILLED CARBONATE POLYMER BLEND COMPOSITIONS  <b>(57) Abstract</b>  Blends of (a) a carbonate polymer component and (b) a monovinylidene aromatic copolymer component not containing a grafted rubber polymer component and (c) an inorganic filler component are prepared having improved combinations of processability, resistance to linear thermal expansion and low temperature toughness. Specifically shaped, small particle size fillers (c) are preferably employed which provide the resistance to linear thermal expansion and maintain the impact resistance of the filled blend.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## FILLED CARBONATE POLYMER BLEND COMPOSITIONS

The present invention relates to filled polymer blend compositions comprising a carbonate polymer, a monovinylidene aromatic copolymer and an inorganic filler. It has unexpectedly been found that these blends are surprisingly easy to process and possess an  
5 unexpectedly improved combination of modulus (stiffness) and linear thermal expansion resistance while maintaining a good, cost effective balance in other categories of physical properties including weatherability, surface aesthetics, heat resistance and toughness. These compositions are particularly useful in the preparation of molded objects, particularly large parts prepared by injection molding techniques and requiring good combinations of these  
10 types of properties. Such properties are particularly desired for the production of injected molded automobile mirror housings, cowl vent grills and instrument panels or instrument housings such as for power tools or telephones.

The utilization of carbonate polymer blends in some applications has typically been accompanied by some undesired effects due to the fact that these polymers have a  
15 relatively high coefficient of linear thermal expansion (CLTE). The CLTE value reflects the tendency of a material to undergo dimensional changes due to thermal fluctuations, especially when in the form of larger molded or extruded articles. For example, if an instrument panel of an automobile expands or contracts excessively in extremely hot or cold conditions it might result in buckling or misfit in the assembled finished product, squeaking and/or stress  
20 fracturing at the point of fastening. Otherwise, there must be sufficient compensation in the product construction or fastening device for the expansion and contraction of the part.

In applications such as interior automotive parts, it is also desirable to provide low temperature impact resistance. While it is possible to provide improved heat resistance, modulus and coefficients of linear thermal expansion in carbonate polymer blends by the  
25 incorporation of increased amount of fillers, toughness, particularly low temperature dart impact resistance, is often reduced to unacceptable levels by fibrous fillers. Currently, glass-filled copolymers of styrene and maleic anhydride (SMA) are one of the materials most often used for injection molding high modulus automobile instrument panels. These materials are sufficiently stiff and heat resistant to perform in this function but typically are brittle and have  
30 breakage problems during installation and/or transportation and have an unacceptable surface for non-covered applications. Moreover, fibrous reinforcing additives such as glass fiber are anisotropic in nature and very efficient in lowering the CLTE in the flow direction but not in the cross flow direction. These additives are also known to cause excessive wear in processing and molding equipment.

35 In the past, various techniques have been employed in attempting to prepare or modify filled carbonate polymer blends to reduce or eliminate these limitations and make these polymers suitable for a wider range of applications. In EP 135,904 it is shown that specified blends of poly(ethylene terephthalate), carbonate polymer and grafted rubber

impact modifiers have good combinations of impact strength and resistance to warpage when containing talc filler. U.S. Patent 4,098,734 discloses blends comprising a matrix interpolymer, a grafted rubber copolymer, a polymer other than the two foregoing polymers having a solubility parameter in the range of 8.5 to 13 and an inorganic filler. U.S. Patent 4,763,133 discloses, as a layer in multilayer laminate antenna structure, blends of certain thermoplastic resins with inorganic fillers, including glass fiber, talc or clay. The filler is added to lower the coefficient of linear thermal expansion while raising the flexural modulus. Carbonate polymer is listed among the numerous thermoplastic resins alleged to be suitable for use in this layer of the laminate.

U.S. Patent 3,424,703 discloses that from 0.025 to 0.5 weight percent silica or talc fillers with a particle size up to 10 micrometers can be incorporated into aromatic polycarbonates to provide thin, relatively haze-free films with a low coefficient of linear thermal expansion.

In JP 52-63,954 (1977) there are disclosed blends composed of 20 to 45 weight percent of an ABS resin, 45 to 20 weight percent of a polycarbonate resin and from 5 to 30 weight percent talc. In JP 138,550 (1987) polybutylene terephthalate is added to polycarbonate/inorganic filler (for example, talc) blends to attempt to improve toughness. In U.S. Patent 5,091,461, it is shown that specified talc fillers, having the proper small size and plate shape provide specific blends of carbonate and rubber modified vinyl aromatic polymers with good combinations of CLTE, toughness and resistance to heat distortion.

While the use of rubber impact modifiers in these types of carbonate/monovinylidene aromatic copolymer blends is known and helps improve or maintain the toughness, it is known that product cost, heat resistance, modulus, weatherability and processability, can be adversely affected. On the other hand, as noted in JP 51-70,992 (1976), it has also been found that carbonate/monovinylidene aromatic copolymer blends that do not contain a rubber component are very difficult to process into standard pellets and shaped or extruded articles due to the tendency of these polymer to exhibit die swell upon their extrusion from the die orifice.

In view of the continuing need for improved combinations of properties in engineering thermoplastics, it would be desirable if there were provided a filled polymeric blend with improved combinations of cost, processability, surface aesthetics and physical properties including CLTE, modulus, impact resistance (especially at low temperatures), weatherability and resistance to heat distortion.

According to the present invention there is now provided such filled polymer blend compositions comprising (a) a carbonate polymer component; (b) a monovinylidene aromatic copolymer not containing a grafted rubber polymer component; (c) an inorganic filler which has a number average particle size less than or equal to 10 micrometers ( $\mu\text{m}$ ) and an average diameter to thickness ratio (D/T) of from 4 to 30; the carbonate polymer component

optionally comprising (a)(1) a rubber polymer impact modifier component. Preferably, these filled polymeric blend compositions comprise (a) carbonate polymer in an amount of from 50 to 95 percent by weight based on weight of components (a) and (b); (b) monovinylidene aromatic copolymer in an amount of from 5 to 50 percent by weight based on weight of components (a) and (b); and (c) inorganic filler in an amount of from 1 to 17 percent by weight based on weight of components (a), (b) and (c).

One embodiment of the present invention is a filled polymer blend composition comprising (a) a carbonate polymer component containing a rubber polymer component; (b) a monovinylidene aromatic copolymer not containing a grafted rubber polymer component and (c) an inorganic filler. Another embodiment of the present invention is a filled polymer blend composition comprising (a) a carbonate polymer component; (b) a monovinylidene aromatic copolymer; (c) an inorganic filler and no grafted rubber polymer component. In a specific preferred embodiment, the inorganic filler is selected from the group consisting of talc, clay and mixtures thereof.

It has been observed that inorganic fillers, particularly talc- and clay-type fillers, preferentially locate in the monovinylidene aromatic copolymer phase of polycarbonate/monovinylidene aromatic copolymer blends and proper selection of the the monovinylidene aromatic copolymer can be used to provide optimized blend properties. A key aspect in the preparation of the improved blends according to the present invention is the use of a relatively high molecular weight monovinylidene aromatic copolymer that does not contain a rubber component, preferably a copolymer with an ethylenically unsaturated nitrile monomer, to produce an excellent combination of properties in carbonate polymer blends containing an inorganic filler.

It has also been found that comonomer content in the monovinylidene aromatic copolymer can be adjusted to further optimize the balance of physical properties. The monovinylidene aromatic copolymer content in the blend can also be adjusted in connection with the inorganic filler content to provide desired balances in the physical properties such as heat resistance, CLTE and resistance to die swell. Surprisingly it has been found that toughness and impact resistance can be maintained in blends according to the present invention, without relying on a rubber-containing impact modifier component. Such blends are therefore particularly valuable since impact modifiers tend to increase product cost and can result in poor modulus, CLTE, heat resistance and weatherability.

In a further embodiment the present invention is also an improved process for reducing the die swell in processes for preparing extruded articles or pellets from carbonate polymer/monovinylidene aromatic copolymer blends comprising the step of extruding a polymer blend composition as described herein to form an article or a strand which is cut into pellets.

In general, monovinylidene aromatic copolymers are well known and commercially available. As is known, such copolymers comprise polymerized therein one or more monovinylidene aromatic monomer and one or more copolymerizable ethylenically unsaturated comonomers, the relative amounts of each being determined by desired polymer properties and cost. In particular, styrene is the most frequent monovinylidene aromatic monomer employed commercially and is a preferred monovinylidene aromatic monomer. Other commercially available monovinylidene aromatic monomers include lower alkyl-substituted (from 1 to 4 carbon atoms) and halogen-substituted styrenes, where the substitution can be on the vinylidene moiety (for example, alpha methyl styrene) or on the aromatic ring such as one or more of the vinyl toluenes or t-butyl styrene, and/or ring halogenated styrenes.

The monovinylidene aromatic copolymer molecular weight was found to play a key role in achieving improved physical properties such as dart impact resistance, tensile strength and elongation. The monovinylidene aromatic copolymers suitably employed according to the present invention are preferably relatively high molecular weight monovinylidene aromatic copolymers. As used herein with regard to the monovinylidene aromatic copolymers, the term "molecular weight" of the copolymer refers to the weight average molecular weight (Mw) as measured by gel permeation chromatography using a polystyrene standard. In order to provide adequate levels of toughness and impact resistance, the copolymers suitable for use in the blends according to this invention should have molecular weights of at least 140,000, preferably at least 145,000, and most preferably at least 150,000. In order to obtain the desired levels of melt flow or processability, the copolymers suitable for use in the blends according to this invention should have molecular weights less than or equal to 250,000, preferably less than or equal to 230,000, most preferably less than or equal to 200,000. Techniques to prepare higher molecular weight copolymers of this type are generally known in the art.

As mentioned above, the monovinylidene aromatic copolymers will also contain one or more copolymerizable ethylenically unsaturated monomers (that is, comonomers), preferably a polar comonomer, which comonomers include the ethylenically unsaturated nitrile monomers (such as acrylonitrile, methacrylonitrile and/or fumaronitrile); maleic acid derivatives such as maleic anhydride; alkyl (meth)acrylates such as methylmethacrylate; N-substituted maleimides such as N-phenylmaleimide; or other polymerizable comonomers. Acrylonitrile (AN), methyl methacrylate (MMA) and maleic anhydride (MA) are the comonomers used in most of the commercial monovinylidene aromatic copolymers. The ethylenically unsaturated nitrile monomers and the alkyl (meth)acrylates are particularly preferred comonomers.

The experiments generally show that as the percent comonomer is increased, the tensile strength, dart impact resistance, flexural modulus, and notch sensitivity increase while gloss and, unexpectedly, CLTE are somewhat reduced.

In order to provide adequate levels of impact resistance, CLTE and modulus, the monovinylidene aromatic copolymers suitable for use in the blends according to this invention should contain the selected comonomer(s) in amounts of at least 10 weight percent based on total weight comonomer(s) and monovinylidene aromatic monomer(s), preferably at least 15 weight percent, more preferably at least 18 weight percent, more preferably at least 20 weight percent and most preferably at least 23 weight percent. As discussed in more detail below, it can be particularly important to employ at least 23 weight percent comonomer in the monovinylidene aromatic copolymer where it is intended to incorporate certain optional rubber components in the carbonate polymer component.

In order to obtain desirable modulus, CLTE, impact strength and melt viscosity levels, the copolymers suitable for use in the blends according to this invention should contain the selected comonomer(s) in amounts of less than or equal to 40 weight percent based on total weight comonomer(s) and monovinylidene aromatic monomer(s), preferably less than or equal to 37 weight percent, more preferably less than or equal to 35 weight percent, and most preferably less than or equal to 33 weight percent. The balance of such monovinylidene aromatic copolymers would obviously be the selected monovinylidene aromatic monomer(s). Highly preferred copolymers contain from 65 to 85 percent styrene monomer and 15 to 35 percent ethylenically unsaturated nitrile monomer.

In general, the monovinylidene aromatic copolymer is employed in amounts to improve the processability of the blend composition and maintain the desired physical properties. The monovinylidene aromatic copolymer is typically incorporated into the blend of the present invention in amounts of at least 5 weight percent, preferably at least 7 weight percent, more preferably at least 10 weight percent and most preferably at least 15 weight percent, said weight percentage being based on weight of carbonate polymer and monovinylidene aromatic copolymer components.

In order to generally maintain the resin blend physical properties the monovinylidene aromatic copolymer is typically incorporated into the blend of the present invention in amounts up to and including 45 weight percent, preferably 40 weight percent, more preferably 30 weight percent and most preferably 25 weight percent based on total weight of the carbonate polymer, monovinylidene aromatic copolymer and, if used, rubber components.

With regard to the upper limits for the monovinylidene aromatic copolymer content, it has been found that the compositions according to the invention begin to lose some of the optimized property combinations as the monovinylidene aromatic copolymer content is increased to the point where its phase volume is sufficiently large that it starts to become

co-continuous with the carbonate polymer phase. As known to those skilled in this area, as the phase volume of a dispersed monovinylidene aromatic copolymer component in a polycarbonate blend increases, there is a transition from dispersed particles or domains of the minor component through a co-continuous morphology where no single phase is dominant.

5 At this point, it has been found that several of the desired properties of the polycarbonate blend, such as heat resistance and impact resistance, begin to diminish unacceptably.

It has subsequently been found that in the case of the carbonate polymer/monovinylidene aromatic copolymer blends according to the present invention, where the inorganic filler locates preferentially in the monovinylidene aromatic copolymer,

10 such as with talc- and clay-type fillers, this correspondingly increases the monovinylidene aromatic copolymer volume. The contents of these two components, therefore, need to be balanced appropriately. In this regard, in the preferred embodiments of the present invention, it has been found that the total volume of the two components should not exceed 45 weight percent for optimized property combinations in the blends, and preferably is less than 40

15 weight percent, more preferably less than 38 weight percent and most preferably less than 33 weight percent.

As mentioned above, the compositions according to the invention do not contain a grafted rubber component in the monovinylidene aromatic polymer phase, and in one embodiment, preferably contain no grafted rubber component at all, in order to obtain

20 improved combinations of desired properties. If desired to further improve the notch sensitivity and/or low temperature impact resistance, it is possible to use an ungrafted rubber polymer impact modifier or a grafted rubber polymer impact modifier component selected such that it will locate in the carbonate polymer component. Preferably any rubber polymer impact modifier will locate in the carbonate polymer component, most preferably only in the

25 carbonate polymer component. If a rubber polymer impact modifier component is employed, it is preferably one or more of the various known types of rubber materials.

In general, such rubber materials have elastic properties and have glass transition temperatures ( $T_g$ 's) less than 0°C, generally less than -10°C, preferably less than -20°C and more preferably less than -30°C. Suitable rubbers include the well known homopolymers and

30 copolymers of conjugated dienes, particularly butadiene; as well as other rubbery polymers such as olefin polymers, particularly copolymers of ethylene, propylene and optionally a nonconjugated diene; or acrylate rubbers, particularly homopolymers and copolymers of alkyl acrylates having from 4 to 6 carbons in the alkyl group. In addition, mixtures of the foregoing rubbery polymers may be employed if desired. Preferred rubbers are homopolymers of

35 butadiene and copolymers thereof with up to 30 percent by weight styrene. Such copolymers may be random or block copolymers and in addition may be hydrogenated to remove residual unsaturation. Also preferred are rubbery polymers prepared from mono-olefins with optional



nonconjugated diene monomers due to their resistance to weathering as compared to conjugated diene rubbers.

Where incorporated, the rubbers are preferably grafted with an amount of a graft polymer or selected based on their composition such that they will be located in the carbonate polymer phase. As taught in U.S. Patent 5,087,663, the selection of comonomer type and amount for the monovinylidene aromatic copolymer and grafted rubber composition helps determine whether a selected grafted rubber component will locate in the carbonate polymer phase and/or at the interface of the two phases during the melt mixing of the components.

As used herein, the terms "located in the carbonate polymer phase" and "not located in the monovinylidene aromatic polymer phase" mean that when the polymer blend is examined, most suitably by transmission electron photomicrograph, the dispersed particles or domains of rubber are completely or mostly surrounded by carbonate polymer. Although some of the rubber particles or domains may be at or very near the interface of the carbonate polymer and monovinylidene aromatic copolymer phases, and possibly contacting the monovinylidene aromatic copolymer, the benefits of the present invention are obtained where the major portion, preferably all, of any rubber phase volume is located in the carbonate polymer phase.

Preferably, the optionally grafted rubber polymer impact modifier is a grafted homopolymer or copolymer of butadiene which is grafted with a polymer of styrene and methyl methacrylate. Along the lines of U.S. Patent 5,087,663, a butadiene rubber component that is grafted with a polymer of styrene and methyl methacrylate, is located preferentially in the carbonate polymer provided that the monovinylidene aromatic copolymer contains at least 23 weight percent ethylenically unsaturated nitrile monomer, preferably at least 25 weight percent, these weight percentages being based upon weight of monovinylidene aromatic monomer(s) and comonomer(s) in the monovinylidene aromatic copolymer. If the optionally grafted rubber polymer component is desired to be used in the blends according to the present invention, those skilled in this area will be able to recognize or prepare other rubber compositions and/or monovinylidene aromatic copolymer compositions that result in the required location of the rubber component in the carbonate polymer phase of the blends according to the present invention.

Some of the preferred rubber-containing materials of this type are the known MBS-type core/shell grafted copolymers having a Tg less than 0°C and a rubber content greater than 40 percent, typically greater than 50 percent. They are generally obtained by graft polymerizing styrene and methylmethacrylate and/or equivalent monomers in the presence of a conjugated diene polymer rubber core, preferably a butadiene homo- or co-polymer. The grafting monomers may be added to the reaction mixture simultaneously or in sequence, and,

when added in sequence, layers, shells or wart-like appendages can be built up around the substrate latex, or core. The monomers can be added in various ratios to each other.

The carbonate polymer resins usefully employed according to the present invention are those previously known and described in the prior art. As known, such resins include the carbonate resins obtained by the interfacial, melt or solution polymerization of a dihydroxy monomer compound, preferably a dihydroxyaryl compound, such as a bis-dihydroxyaryllalkane or preferably a dihydroxy silicon-containing compound, with a polycarbonate precursor such as phosgene, a bischloroformate or a dicarbonate such as diphenyl carbonate or dimethyl carbonate. Examples of suitable dihydroxy silicon-containing compounds are shown in U.S. Patents 3,189,662; 3,419,634; 3,821,325; 4,584,360 and 5,310,793 which are incorporated by reference with regard to such monomers. Preferably the carbonate polymer is an aromatic carbonate polymer, more preferably it is prepared from an aromatic diol such as bisphenol A, tetrabromo-bisphenol A, tetramethyl bisphenol A, 1,1-bis(4-hydroxyphenyl)-1 phenylethane, bis(hydroxyphenyl)fluorene or mixtures of two or more of these.

In addition to the suitable polycarbonates prepared by exclusive use of one or more of the above diols, carbonate polymers suitable for use according to the claimed invention could be prepared in the presence of an amount of a diacid or diacid chloride to produce the known poly(ester-carbonates).

The carbonate polymers suitable for use in the present invention include a broad range of the known carbonate polymers in terms of molecular weight or melt flow rate (which is an indirect indication of resin molecular weight). In general, to obtain the desired processability, the carbonate polymer molecular weight should provide a resin melt flow rate (MFR) of at least 0.1 grams per 10 minutes (g/10 min) by ASTM 1238-35, condition O, preferably at least 0.5 g/10 min, more preferably at least 1 g/10 min, and most preferably at least 3 g/10 min. In order to provide the desired level of physical properties, including toughness, the carbonate polymer molecular weight should provide a resin melt flow rate (MFR) of less than 80 g/10 min, preferably less than 40 g/10 min, more preferably less than 30 g/10 min, and most preferably less than 20 g/10 min.

These carbonate polymers are employed in the blends according to the invention in amounts sufficient to provide the desired levels of toughness and resistance to heat. In general the carbonate polymer is employed in an amount of at least 55, preferably at least 60, more preferably at least 70 and most preferably at least 75 percent by weight based on weight of carbonate and monovinylidene aromatic polymers and, if used, rubber. Usually, with these considerations in mind, the carbonate polymer is employed in an amount of up to and including 95, preferably up to and including 90 and more preferably up to and including 85 percent by weight based on weight carbonate and monovinylidene aromatic polymers and, if used, rubber.

It has been found that recycled carbonate polymer, which normally is somewhat more brittle than virgin resin, can suitably be employed in the carbonate polymer in compositions according to the present invention in amounts up to 75 weight percent based on carbonate polymer, preferably up to 50 weight percent, without experiencing unacceptable  
5 brittleness in the blend.

In general, the blends according to the present invention can incorporate talc, clay or a similar type of filler which has a number average particle size less than or equal to 10 micrometers ( $\mu\text{m}$ ) and an average diameter to thickness ratio (D/T) of from 4 to 30 and provides the desired levels of physical and other property requirements such as toughness, modulus  
10 (stiffness) and resistance to linear thermal expansion. Several varieties of talc and clay filler materials have been found to be especially suitable.

As disclosed in U.S. Patent 5,091,461, elongated or plate-shaped fillers having the specified small particles have been found to better maintain the toughness properties of resin blends as compared to fibrillar or spherical shaped fillers. The relevant portions of U.S. Patent  
15 5,091,461 relating to the disclosed talc fillers are hereby incorporated by reference herein. The suitability of the filler in maintaining the preferred levels of impact resistance of molded articles prepared from the resin has been found to be a function of the average diameter/thickness ratio (D/T) of the filler particles together with obtaining a uniformly small particle-sized filler. Highly preferred are those compositions incorporating fillers having an  
20 average diameter/thickness ratio (D/T) as measured according to the below-described technique of at least 4, preferably at least 6, more preferably at least 7. With regard to the maximum level for the D/T ratio, it has been found desirable to have a value up to and including 30, preferably up to and including 24, preferably up to and including 18, more preferably up to and including 13, and most preferably up to and including 10.

For determining the D/T ratio, the diameter (or longest dimension) of the fillers as  
25 well as their thickness (shortest dimension of the 2 dimensions measurable) can be measured by preparing a filler modified polymeric resin sample and measuring the particle dimensions of the dispersed particles on electron photomicrographs of thin sections of the polymers. The electron photomicrograph should have a magnification of from 3000X to 15000X, preferably  
30 7500X. By physically measuring the diameter/thickness of a representative sample of at least 25 and preferably at least 50 filler particles, one can obtain a relatively accurate value for the diameter/thickness ratio.

The inorganic fillers preferably employed according to the present invention are the known mineral talcs and clays. Preferred are the uncalcined talcs and clays having very low  
35 free metal oxide content. Talcs and clays are generally known fillers for various polymeric resins. See for example U.S. Patents 5,091,461 and 3,424,703 and EP 391,413, where these materials and their suitability as filler for polymeric resins are generally described.

The mineral talcs best suited are hydrated magnesium silicates as generally represented by the theoretical formula:



Compositions of talcs may vary somewhat with locality in which they are mined. Montana talcs,  
5 for example, closely approach this theoretical composition. Suitable mineral talcs of this type are commercially available as Microtalc MP 25-38 and Microtalc MP 10-52 from Pfizer.

The clays best suited for use are hydrous alumino silicate-type compounds, generally represented by the formula:



10 Suitable clay materials are commercially available as Tex 10R brand clay from Anglo American Clay Co.

As is disclosed in U.S. Patent 5,091,461, elongated or plate-shaped fillers having the specified uniformly small particles have been found to better maintain the toughness properties of resin blends as compared to fillers which are spherical shaped and/or have larger  
15 particles. To similarly obtain the most preferred polymeric blends according to the present invention it is desirable to employ specific fillers where the particles have a very small average particle size and have a relatively narrow particle size distribution. As used herein, the "average particle size" and "maximum particle size" are measured by Coulter Counter techniques. As known to those skilled in the art, Coulter Counter techniques measure these  
20 values based on volume and give an equivalent spherical volume diameter meaning that the diameter readings are diameters that would be observed for spheres having the same volume as the plate shaped particles. Therefore, if measuring the filler particle sizes by other techniques, very slightly different values could be observed.

Thus, the carbonate polymer compositions included within the scope of this  
25 invention generally utilize such inorganic fillers with a number average particle size as measured by Coulter Counter of less than or equal to 10 micrometers ( $\mu\text{m}$ ) preferably less than or equal to 3  $\mu\text{m}$ , more preferably less than or equal to 2  $\mu\text{m}$ , more preferably less than or equal to 1.5  $\mu\text{m}$  and most preferably less than or equal to 1.0  $\mu\text{m}$ . Depending upon the grinding or preparation technique, such fillers can have number average particle sizes of at least 0.05  $\mu\text{m}$ ,  
30 preferably at least 0.1  $\mu\text{m}$ , and more preferably at least 0.5  $\mu\text{m}$ . In general, the smaller average particle sizes, if available, could very suitably be employed but it has been found difficult to commercially obtain fillers of this type having an average particle size less than 1.5  $\mu\text{m}$ .

In addition to having the specified small average particle size, it has also been found to be important in optimizing the filled blend impact properties to provide uniformly  
35 small particle-sized fillers where the number or amount of larger particles ("maximum particle size") is reduced. In this regard, preferred maximum particle size specifications have been determined for the most preferred fillers used in the blends according to the invention. Suitable fillers generally have a maximum particle size less than or equal to 50  $\mu\text{m}$ , preferably

less than or equal to 30  $\mu\text{m}$ , more preferably less than or equal to 25  $\mu\text{m}$ , more preferably less than or equal to 20  $\mu\text{m}$  and most preferably less than or equal to 15  $\mu\text{m}$ .

Another way of specifying the desired uniform small particle size and particle size distribution of the fillers preferably used in the practice of the present invention is to specify that at least 98 weight percent, preferably at least 99 weight percent, of the particles thereof in final blend have an equivalent spherical volume diameter less than 44  $\mu\text{m}$ , preferably less than 20  $\mu\text{m}$ . The weight percentage of the filler particles having such diameters can similarly be measured by particle size analysis with a Coulter Counter.

In preparing the carbonate polymer compositions according to the present invention and obtain optimized combinations of toughness, stiffness and resistance to thermal linear expansion, it has been found generally desirable to employ filler in an amount of at least 1, preferably at least 3 and more preferably at least 5 percent by weight based on weight of filler, carbonate polymer, monovinylidene aromatic polymer and optional rubber. Usually it has been found sufficient to employ an amount of filler up to and including 20, preferably 15, more preferably 12 and most preferably 10 percent by weight, which weight percentages are based on weights of filler, carbonate polymer, monovinylidene aromatic polymer and optional rubber. As mentioned above, where the inorganic filler locates preferentially in the monovinylidene aromatic copolymer, such as with talc- and clay-type fillers, this correspondingly increases the monovinylidene aromatic copolymer volume. The contents of these two components, therefore, need to be balanced appropriately. In this regard, in the preferred embodiments of the present invention, it has been found that the total volume of the two components should not exceed 45 weight percent for optimized property combinations in the blends, and preferably is less than 40 weight percent, more preferably less than 38 weight percent and most preferably less than 33 weight percent.

With regard to obtaining optimized properties in articles prepared from the blend resins, it has been found that extremes in temperature conditions can result in poor fitting of various components of the finished assembly unless the coefficient of linear thermal expansion, as measured according to ASTM D-696 in units of inch per inch per  $^{\circ}\text{F}$  (in/in/ $^{\circ}\text{F}$ ) or millimeter per millimeter per  $^{\circ}\text{C}$  (mm/mm/ $^{\circ}\text{C}$ ) is less than  $3.7 \times 10^{-5}$  in/in/ $^{\circ}\text{F}$  ( $6.7 \times 10^{-5}$  mm/mm/ $^{\circ}\text{C}$ ), preferably less than  $3.5 \times 10^{-5}$ / $^{\circ}\text{F}$  ( $6.3 \times 10^{-5}$ / $^{\circ}\text{C}$ ), and more preferably less than  $3.3 \times 10^{-5}$ / $^{\circ}\text{F}$  ( $5.6 \times 10^{-5}$ / $^{\circ}\text{C}$ ), over the temperature range of  $-22$  to  $185^{\circ}\text{F}$  ( $-30$  to  $85^{\circ}\text{C}$ ).

It has surprisingly been found that injection molded components prepared from the resin blends of the present invention generally have an exceptionally smooth, reduced gloss, defect-free surface finish. These features, together with the improved combinations of resistance to linear thermal expansion, modulus, heat resistance and toughness make these resins desirable for many applications such as injection molding, extrusion and blow molding of the resins into desirable shaped articles. In addition, extruded materials can be readily thermoformed into desired shaped articles.

The compositions according to the present invention are prepared by blending the foregoing components according to known blending and mixing techniques. Desirably the components may be first mixed or dry blended prior to melt blending in an appropriate extruder or other melt blending device, preferably under vacuum for complete water and volatile removal. The components may be combined and blended in any order. In order to improve the mixing of fine, powdery fillers into the polymer blend compositions, it may be desirable to initially mix the filler with a polymer component having a similarly fine and powdery consistency, if possible. In this regard, grinding of one of the polymer components may be desired if not already available in such form.

10

In addition to the foregoing components, additional additives may be included in the blend as long as they do not substantially deleteriously affect the other physical properties of the composition. Such additional additives may include, for example, pigments; light stabilizers such as U.V. absorbers; antioxidants; processing aids such as internal lubricants and mold release agents such as waxes; flame and drip retardants; filler coupling agents, for example the polyfunctional organosilicon compounds disclosed in U.S. Patent 4,528,303 and other additives.

Having described the invention the following examples are provided as further illustrative and are not to be construed as limiting. Parts and percentages are based on weight.

20

As shown in the following tables, a series of filled carbonate polymer/- amount, carbonate polymer and monovinylidene aromatic polymer. In addition to the components shown in the following tables, the blends also contained standard antioxidants and used epoxidized soybean oil (ESO) to tackify the resin pellets to facilitate the combination of powdery additives such as the filler.

25

The carbonate polymer resins are mostly commercially available grades of Calibre (TM) brand, bisphenol A-based polycarbonate (PC) produced by The Dow Chemical Company. The melt flow rates (MFR) are measured in grams per 10 minutes (g/10 min) according to ASTM D-1238, condition O while the weight average molecular weight values (Mw) are measured by gel permeation chromatography using a polystyrene standard.

30

Table 1 - Carbonate Polymers

	<u>MFR</u>	<u>M<sub>w</sub></u>	<u>Trade Name</u>
PC-10	10	28,400	CALIBRE* 300-10
PC-13	13	26,800	CALIBRE* 300-15
PC-14	14	26,300	CALIBRE* 300-15
PC-20	20	22,000	CALIBRE* 300-20
Ground Flake	14	26,000	

35

The monovinylidene aromatic copolymer resins identified in the following table are copolymers of styrene and acrylonitrile (referred to below as "SAN") and are a mixture of experimental and commercially available products.

Table 2 - Monovinylidene Aromatic Copolymer Components

No.	Description	Mw	Wt% AN
SAN-1	Poly(styrene/acrylonitrile)	278,000	6% AN
SAN-2	Poly(styrene/acrylonitrile)	174,000	16% AN
SAN-3	Poly(styrene/acrylonitrile)	170,000	20% AN
SAN-4	Poly(styrene/acrylonitrile)	150,000	25% AN
SAN-5	Poly(styrene/acrylonitrile)	175,000	30% AN
SAN-6	Poly(styrene/acrylonitrile)	80,000	31% AN
SAN-7	Poly(styrene/acrylonitrile)	95,000	31% AN
SAN-8	Poly(styrene/acrylonitrile)	135,000	31% AN
SAN-9	Poly(styrene/acrylonitrile)	142,000	39% AN
ABS-1*	Poly(styrene/acrylonitrile) containing about 20 weight percent butadiene polymer rubber grafted with SAN	155,000 (SAN)	28% AN (in SAN)

\*Monovinylidene aromatic copolymer not suitable for use according to the present invention

As indicated, a butadiene rubber-modified copolymer of styrene and acrylonitrile (referred to herein as ABS or an ABS-type resin) was used to provide control blends where a grafted rubber polymer component was located in the monovinylidene aromatic copolymer. Transmission electron microscopy of OsO<sub>4</sub> and RuCl<sub>4</sub> stained samples is used for visual determination of which phase contains the rubber particles. The ABS resin was a mass solution polymerized ABS and contained the indicated amounts of (B) SAN including both ungrafted and grafted polymer and (D) butadiene rubber which level does not include grafted SAN. The SAN and Rubber levels were determined by the relative amounts of rubber and monomers incorporated during production of the ABS resin.

In several of the compositions that were prepared, amounts of an optional core shell grafted rubber components were incorporated. There are small monovinylidene aromatic copolymer (MVAC) components in Copolymers 1 and 2 comprising styrene, methyl methacrylate and small amounts of other crosslinking and proprietary comonomers, which are substantially completely graft polymerized to the rubber. According to information from the supplier, these materials contained the below indicated levels of rubber and methylmethacrylate (MMA).

In several of the compositions that were prepared a methyl methacrylate grafted ethylene-carbon monoxide rubbery component ("Copolymer 3") was incorporated. This product is a graft copolymer composed of a substrate copolymer of 90 weight percent ethylene and 10 weight percent carbon monoxide which is then grafted with 20 weight percent of a mixture of methyl methacrylate (94 wt%) and methyl acrylate (6 wt%) generally according to the process shown in USP 5,079,316.

**Table 3 - Optional Rubber Polymer Materials**

	MVAC Level (wt %)	MMA Comonomer Content in MVAC (wt %)	Rubber Level (wt %) and Type
Core/Shell MBS Copolymer 1	28	about 40	72 Butadiene
Core/Shell Copolymer 2* Paraloid 3339	22	estimated to be about 90	78 Butyl Acrylate
Copolymer 3 MMA-grafted ECO	0	N/A	80 Ethylene/ Carbon monoxide

\*Commercially available from Ameri-Haas as Paraloid 3339

The talc filler used in the experiments was the commercially available mineral talc Microtalc MP 10-52 available from Pfizer identified below. Chemically this material is a hydrated magnesium silicate as represented by the formula:





For this filler, shape and ratio of the diameter to the thickness of the filler particles (D/T) were determined by preparing a filler modified polymeric resin sample, and preparing transmission electron photomicrographs (TEM's) of thin sections of the polymers at magnifications in the range of 3,000 to 15,000 X. Then shapes and sizes were determined by physically measuring the diameters and thicknesses for a representative sample of at least 25 filler particles and computing their ratio. The number average particle size and maximum particle size in micrometers ( $\mu\text{m}$ ) ("Ave. Particle Size" and "Max. Particle Size", respectively) are approximates ( $\pm 5\%$ ) and were determined by Coulter Counter analysis. The weight percentages of particles in the blend having a diameter less than  $44 \mu\text{m}$  and less than  $20 \mu\text{m}$  ("Wt % <  $44 \mu\text{m}$ " and "Wt % <  $20 \mu\text{m}$ ") are also measured by Coulter Counter.

For comparison purposes, a glass fiber filler, Owens Corning OCF 415 brand fiber, was employed in an otherwise similar blend.

Table 4 - Inorganic Fillers

Type	Trade Name	Shape	D/T	Ave. Particle Size ( $\mu\text{m}$ )	Max. Particle Size ( $\mu\text{m}$ )	Wt % < $20 \mu\text{m}$	Wt % < $40 \mu\text{m}$
Talc	Microtalc MP 10-52	Plate	9.0	0.9	10	100	100
Glass Fiber	Owens Corning OCF 415	Fiber					

The amount of talc in the blend product was confirmed to correspond to the predetermined incorporation levels by a combustion analysis where all organic matter in the sample is burned away and the remaining inorganic component weighed. The results of this analysis, the weight percent talc based on total composition weight, are shown as "Percent Talc Ash" in the data tables.

In addition, all of the Experimental Compositions contained Monarch 800 brand carbon black, a commercially available product from Cabot.

The components to be blended were dry blended and melt mixed under 20 to 27 inches of vacuum at  $270^\circ\text{C}$  on a 30 mm Werner-Pfleiderer co-rotating, twin screw extruder at a speed of 250 rpm. The heaters were maintained at  $518^\circ\text{F}$  ( $270^\circ\text{C}$ ) and the throughput rate was 30 to 40 lbs/hour (13.6 Kg/hr). Each extruded composition was passed through a water bath, chopped into granules and collected for molding. Granules were thoroughly dried in a circulated air oven at  $110^\circ\text{C}$  for 4 to 6 hours prior to molding. All samples were prepared by injection molding on a 75 ton Arburg brand molding machine. Molding temperatures for the barrel were set at  $270^\circ\text{C}$  to  $290^\circ\text{C}$  while the mold temperature was set at  $150^\circ\text{F}$  to  $160^\circ\text{F}$  ( $66$  to  $71^\circ\text{C}$ ).

The physical properties of the resulting injection molded samples were then measured using standard ASTM test procedures. Test results are shown in the Tables. ASTM D-696 was used to measure the coefficient of linear thermal expansion (CLTE) and the results are reported as  $\times 10^{-5}/^{\circ}\text{C}$  (and  $\times 10^{-5}/^{\circ}\text{F}$ ). Dart impact strength is measured according to ASTM D-3763-86 at  $23^{\circ}\text{C}$  and is reported in inch pounds (In Lbs) and Joules (J).

Izod impact resistance values were obtained according to ASTM D-256 at  $23^{\circ}\text{C}$  using an Izod impact tester and are reported in inch pounds (In Lbs) and Joules (J). Notched samples were notched with a low speed notcher equipped with a 9.6 mil cutting wheel. Unnotched weldline Izod impact resistance values were obtained using samples cut from the middle of a double gated tensile bar and tested on an Izod impact tester and are reported in inch pounds (In Lbs) and Joules (J). Except where stated otherwise, the specimen thickness was 0.125 inches (3.12 mm) and the impact velocity was 200 meters/minute (8,000 inches/min).

Tensile tests (Tens Strgth Yield) were made using an Instron brand tensile tester according to ASTM D-638 at a single strain rate of 2 inch/min and the results are reported in pounds per square inch (PSI) and megaPascals (MPa). The flexural modulus (Flex Modulus) of the samples was also tested on the Instron tester at 0.2 inch/min (according to ASTM D-790) and the results are reported in pounds per square inch times 1000 (psi X 1,000) and megaPascals (MPa). The melt flow rate values (MFR) reported below were measured according to ASTM D-1238-85 at  $265^{\circ}\text{C}$  with a 3.8 kilogram weight and are reported in grams per ten minutes (gr/10 min). The heat distortion temperature under load (DTUL) is measured according to ASTM D-648-82 on a Tinius Olsen Heat Distortion Apparatus and is reported in  $^{\circ}\text{F}$  and  $^{\circ}\text{C}$ .

The Die Swell findings reported below were obtained by visual observation of the molten polymer blend strand during extrusion, the presence of die swell making it extremely difficult to maintain a uniform strand during extrusion. The surface quality is determined visually with the aid of a magnifying glass, with Good ("G") indicating smooth and Poor ("P") indicating rough.

The ultraviolet radiation resistance of the compositions ("UV Resistance") containing no diene rubber is expected to be good ("G") while diene rubber containing compositions would have poorer ("P") UV resistance.

Table 5 - Effect of Filler and Monovinylidene Aromatic Copolymer

		Control 1*	Control 2*	Control 3*	Control 4*	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
5	PC-10	WtPts Wt %	1183 65	1264 69	1379 69	1264	1264	1264	1264	1264	1264
	PC-20	WtPts Wt %	1820 100								
	ABS-1 (28 % AN)	WtPts Wt %	- 35	-	-	-	-	-	-	-	-
10	SAN-1 (6% AN)	WtPts Wt %	-	-	-	556 31	-	-	-	-	-
	SAN-2 (16% AN)	WtPts Wt %	-	-	-	-	556 31	-	-	-	-
	SAN-3 (20% AN)	WtPts Wt %	-	-	-	-	-	556 31	-	-	-
	SAN-4 (25% AN)	WtPts Wt %	0 0	-	556 31	609 31	-	-	556 31	-	-
15	SAN-5 (30% AN)	WtPts Wt %	-	-	-	-	-	-	-	556 31	-
	SAN-9 (39% AN)	WtPts Wt %	-	-	-	-	-	-	-	-	556 31
	Filler	WtPts Wt %	168 8.4	168 8.4	168 8.4	0 -	168 8.4	168 8.4	168 8.4	168 8.4	168 8.4
	All Talc, except where shown			Glass Fiber							
20	Carbon Black	WtPts Wt %	4 0.2	4 0.2	4 0.2	4 0.2	4 0.2	4 0.2	4 0.2	4 0.2	4 0.2
	CLTE $\times 10^{-5}/^{\circ}\text{F}$ $\times 10^{-5}/^{\circ}\text{C}$		3.11 5.60	3.46 6.23	N/A 6.82	3.18 5.72	3.12 5.62	3.09 5.56	3.02 5.44	2.95 5.31	2.94 5.29
	Dart Impact 23°C (In Lbs) (J)		322 36	413 47	33 4	438 50	77 9	488 56	510 58	510 58	457 52
25	Tens Strgth Yield (psi) (MPa)		9324 64	8324 57	10181 70	10138 70	9985 69	10530 73	10474 72	10298 71	10483 72
	Flex Modulus (psi $\times 1,000$ ) (MPa)		423 2917	416 2868	541 3729	408 2813	430 2965	507 3496	503 3468	517 3565	540 3723
	MFR (gr/10 min)		-	10.3	10.3		9.4	17.3	14.5	15.3	12.4
30	Die Swell		No	No	No	Yes	No	No	No	No	No
	Surface Quality		G	G	P	G	G	G	G	G	G
	UV Resistance		G	P	G	G	G	G	G	G	G

\*Not an example of the present invention

Table 6 - Effect of SAN Molecular Weight

		Ex. 7	Ex. 8	Ex. 9	Ex. 10
	PC-10	1264	1264	1264	1264
	WtPts	69	69	69	69
5	SAN-6 (Mw 80,000)	556	-	-	-
	WtPts	31	-	-	-
	SAN-7 (Mw 95,000)	-	556	-	-
	WtPts	-	31	-	-
	SAN-8 (Mw 135,000)	-	-	556	-
	WtPts	-	-	31	-
	SAN-5 (Mw 175,000)	-	-	-	556
	WtPts	-	-	-	31
10	Talc	168	168	168	168
	WtPts	8.45	8.45	8.45	8.45
	Carbon Black	4	4	4	4
	WtPts	0.2	0.2	0.2	0.2
	SAN Mol Wt (x 1000)	80	95	135	175
	% AN	31	31	31	30
15	CLTE				
	x 10 <sup>-5</sup> /°F	2.96	2.95	2.94	2.92
	x 10 <sup>-5</sup> /°C	5.33	5.31	5.29	5.26
	Dart Impact 23°C				
	(In Lbs)	21	48	98	479
	(J)	2.4	5.5	11.2	54.6
	Izod Impact 23°C				
	Notched (Ft Lbs/in)	0.5	0.7	0.9	1.0
	(J/m)	26.5	37	48	53
20	Izod Impact 23°C				
	Unnotched (Ft Lbs/in)	15.4	20.2	21.8	25.2
	(J/m)	816	1071	1155	1336
	DTUL 66 psi (0.455MPa)				
	°F	255	258	261	261
	°C	124	126	127	127
25	Tens Strgth Yield				
	(psi)	10313	10405	10616	10535
	(MPa)	71	72	73	73
	% Elongation	11	18	27	32
	Die Swell	No	No	No	No
	Surface Quality	G	G	G	G

30

35

Table 7 - Effect of Rubber Location

		Control 2	Control 5	Ex. 11	Ex. 12	Ex. 13
5	PC-10	WtPts Wt%	1183 65	1177 64.5	1177 64.5	1177 64.5
	SAN-2 (16% AN)	WtPts Wt%	- 28.5	- 28.5	- 28.5	- 28.5
	SAN-4 (25% AN)	WtPts Wt%	- 28.5	- 28.5	- 28.5	- 28.5
	ABS-1	WtPts Wt%	637 35	- -	- -	- -
	Core/Shell Copolymer 1	WtPts Wt%	- 7	124 7	- -	- -
10	Core/Shell Copolymer 2	WtPts Wt%	- -	- -	124 7	- -
	MMAgECO Copolymer 3	WtPts Wt%	- -	- -	- -	124 7
	% Rubber	Wt%	7.1	5.0	5.0	5.5
15	~Rubber Tg °C		-80	-80	-80	-40
	Rubber Location		SAN	SAN	PC	PC
	Talc	WtPts Wt%	168 8.45	168 8.45	168 8.45	168 8.45
	Carbon Black	WtPts Wt%	4 0.2	4 0.2	4 0.2	4 0.2
	CLTE x 10 <sup>-5</sup> /°F x 10 <sup>-5</sup> /°C		3.46 6.23	3.47 6.25	3.32 5.98	3.35 6.03
20	Dart Impact 23°C (In Lbs) (J)		413 47	454 52	494 56	448 51
	Izod Impact 23°C (Ft lbs/in) (J/m)		8.1 432	3.7 198	6.1 326	5.9 315
	Flex Modulus (psi x 1,000) (MPa)		416 2868	401 2765	459 3165	440 3034
25	Surface Quality		G	G	G	G
	Die Swell		No	No	No	No

As can be seen in the above tables, monovinylidene aromatic copolymer (SAN) resins containing 6, 16, 20, 25, 31, and 39 percent comonomer (AN) and having roughly the same Mw (150,000-170,000) were evaluated. The evaluation results indicate several trends in physical and rheological properties are present as the percent comonomer is increased from 5 percent to 39 percent. These trends generally show that as the percent comonomer is increased, the viscosity, tensile strength, flexural modulus and notch sensitivity increases while gloss and CLTE is reduced. Practical toughness as measured by dart impact shows an optimum between 16 percent and 31 percent comonomer with very poor results observed on either side. Transmission Electron Micrographs (TEM) appear to indicate the talc is located primarily in the SAN phase at higher comonomer content and in both phases at lower comonomer levels.

In addition, several SAN resins having 31 percent comonomer with molecular weights ranging from 80,000 to 175,000 were evaluated. SAN molecular weight was also found

to play a key role in achieving improved physical properties. For example, dart impact, tensile elongation viscosities all increased as the molecular weight was increased.

Based on these initial results it is believed that a monovinylidene aromatic copolymer resin having between 15 percent and 33 percent comonomer and a molecular weight greater than 140,000 (preferably above 145,000) provides low cost, good surface aesthetics, low CLTE, good UV resistance, easy flow, high modulus, good HDT and good practical toughness in the claimed blends.

In the further experimental compositions shown below, a variety of carbonate polymers are employed, along with a range of other component optionally suited for use in the compositions according to the present invention. Control 6 in Table 12 compares compositions according to the present invention with a commercially available, glass filled styrene maleic anhydride polymer resin commonly used for automotive interior parts.

15

20

25

30

35

Table 8 - Effect of SAN Content

Ex. No.		14	15	16	17
5	PC	1618	1418	1218	1078
	Wt %	89	78	67	57
5	SAN-4	200	400	600	800
	Wt %	11	22	33	43
	Talc	170	170	170	170
	Wt %	8.5	8.5	8.5	8.5
	Carbon Black	4	4	4	4
	Wt %	0.2	0.2	0.2	0.2
10	Izod Impact 23°C Unnotched (Ft Lbs/in)	59.5	56.0	18.4	18.5
	(J/m)	3177	2990	983	988
	Izod Impact 23°C Notched (Ft Lbs/in)	1.6	1.1	0.8	0.7
	(J/m)	85	59	43	36
	Dart Impact				
	23°C (In Lbs)	440	426	55	92
15	(J)	50	48	6	10
	0°C (In Lbs)	475	468	-	-
	(J)	54	53	-	-
	-30°C (In Lbs)	413	295	-	-
	(J)	47	33	-	-
	DTUL 66 psi (0.455 MPa)				
	°F	280	274	263	263
20	°C	136	133	127	127
	DTUL 264 psi (1.82 MPa)				
	°F	255	248	226	224
	°C	123	119	107	106
	Flex Modulus (psi x 1000)	478	501	518	541
	(MPa)	3276	3454	3572	3730
	Tens Strgth Yield (psi)	9624	10025	10595	10536
	(MPa)	66	69	73	73
	Tensile Break (psi)	8877	7762	6892	6391
	(MPa)	61	54	48	44
25	% Elongation	177	167	37	20
	CLTE				
	x 10 <sup>-5</sup> /°F	2.96	2.96	3.07	2.91
	x 10 <sup>-5</sup> /°C	5.33	5.33	5.53	5.24

30

35

Table 9 - Effect of Ground Polymer and Talc Level

		18	19	20	21	16	22	23
PC	WtPts	1432	1392	1352	1322	1218	1492	1392
	Wt %							
PC -14	WtPts	1332	1292	1252	1222		1392	1292
PC GF	WtPts	100	100	100	100		100	100
SAN-4	WtPts	500	500	500	500	600	300	400
	Wt %							
Talc	WtPts	60	100	140	180	170	200	200
	Wt %							
Wt% SAN plus filler		28	30	32	33.5	38.5	25	30
Carbon Black	WtPts	-	-	-	-	4	-	-
	Wt %							
Izod Impact 23°C								
Unnotched	(Ft Lbs/in)	57.6	58.2	53.6	29.2	18.4	52.4	50.7
	(J/m)	3076	3108	2862	1559	983	2798	2707
Izod Impact 23°C								
Notched	(Ft Lbs/in)	1.2	1.0	1.1	0.8	0.8	1.0	1.0
	(J/m)	64	53	59	43	43	53	53
Dart Impact								
23°C	(In Lbs)	460	450	430	407	55	402	413
	(J)	52	51	49	46	6	45	47
0°C	(In Lbs)	498	412	447	316	-	411	411
	(J)	56	47	51	36		46	46
-30°C	(In Lbs)	433	484	244	61	-	362	159
	(J)	49	55	28	7		41	18
DTUL 264 psi (1.82 MPa)								
°F		242	239	236	236	226	253	242
°C		116	114	112	112	107	122	116
Flex Modulus	(psi x 1000)	443	468	492	542	518	506	528
	(MPa)	3055	3227	3392	3737	3572	3489	3641
Tens Strgth Yield	(psi)	10204	10280	10399	10472	10595	10082	10305
	(MPa)	70	71	72	72	73	70	71
Tensile Break	(psi)	8660	7979	7881	7359	6892	7695	6844
	(MPa)	60	55	54	51	48	53	47
% Elongation		199	182	125	32	37	68	45
CLTE								
x 10 <sup>-5</sup> /°F		3.4	3.23	3.11	2.76	3.07	2.96	2.89
x 10 <sup>-5</sup> /°C		6.12	5.81	5.60	4.97	5.53	5.33	5.20

30

35



Table 10 - Effect of PC Molecular Weight

		24	25	26	27	28	29
5	PC	WtPts	1432	1372	1322	1432	1372
		Wt%	78	75	73	78	75
10	PC 14	WtPts	-	-	-	1322	1272
		Wt%	-	-	-	-	-
15	PC 20	WtPts	1322	1272	1222	-	-
		Wt%	-	-	-	-	-
20	PC GF	WtPts	100	100	100	100	100
		Wt%	-	-	-	-	-
25	SAN 4	WtPts	400	450	500	400	450
	25% AN	Wt%	22	25	27	22	25
30	Talc MP 10-52	WtPts	170	170	170	170	170
		Wt%	8.5	8.5	8.5	8.5	8.5
35	Izod Impact 23°C						
	Unnotched (Ft Lbs/in)		40.4	30.4	24.7	55.5	47.3
	(J/m)		2157	1623	1319	2964	2526
40	Izod Impact 23°C						
	Notched (Ft Lbs/in)		0.8	0.8	0.7	1.0	1.0
	(J/m)		43	43	37	53	53
45	Dart Impact						
	23°C (In Lbs)		407	411	408	416	421
	(J)		46	46	46	47	48
50	0°C (In Lbs)		390	387	383	450	425
	(J)		44	44	44	51	48
55	-30°C (In Lbs)		219	153	40	361	309
	(J)		25	17	5	41	35
60	DTUL 264 psi (1.82 MPa)						
	°F		242	239	231	245	240
	°C						
65	Flex Modulus (psi x 1000)		514	520	516	497	513
	(MPa)		3544	3585	3558	3427	3537
70	Tens Strgth Yield (psi)		10191	10271	10382	10138	10299
	(MPa)		70	71	72	70	71
75	Tensile Break (psi)		7600	7247	7536	7536	7425
	(MPa)		52	50	52	52	51
80	% Elongation		28	27	22	101	68
85	CLTE						
	x 10 <sup>-5</sup> /°C		5.33	5.33	5.35	5.22	5.13
	x 10 <sup>-5</sup> /°F		2.96	2.96	2.97	2.90	2.85

Table 11 - Effect of Non-Grafted Rubber

		30	31	32
5	PC	WtPts	1372	1352
		Wt %	75	74
	PC 14	WtPts	1272	1252
		Wt %	75	74
	PC GF	WtPts	100	100
		Wt %	100	100
	SAN 4	WtPts	450	450
		Wt %	25	26
10	Polyethylene 0.87 den		-	20
				60
	Talc MP 10-52	WtPts	170	170
		Wt %	8.5	8.5
	Izod Impact 23°C			
	Unnotched (Ft Lbs/in)	47.3	45.4	59.4
		(J/m)	2526	2424
				3172
	Izod Impact 23°C			
	Notched (Ft Lbs/in)	1.0	1.1	1.5
15		(J/m)	53	59
				80
	Dart Impact 23°C			
	(In Lbs)	421	389	373
		(J)	48	44
				42
	DTUL 264 psi (1.82 MPa)			
	°F	240	237	238
		°C		
20	Flex Modulus (psi x 1000)	513	523	477
	(MPa)	3537	3606	3289
	Tens Strgth Yield (psi)	10299	10024	9578
	(MPa)	71	69	66
	Tensile Break (psi)	7425	6780	6132
	(MPa)	51	47	42
25	% Elongation	68	42	86
	CLTE	x 10-5/°F	2.85	3.17
		x 10-5/°C	5.13	5.71
				5.69
	Rubber Location		PC	PC

30

35

Table 12 - Comparison with Commercial Filled Resin

		33	34	Control 6* Dylark 378-P20 (20% glass filled SMA)
5	PC	WtPts	63.6	63.3
		Wt %	70	70
	PC 10	WtPts	-	59.0
	PC 14	WtPts	59.6	-
	PC GF	WtPts	4.0	4.3
	SAN 5	WtPts	-	27.0
		Wt %	-	30
10	SAN 4	WtPts	27.0	-
		Wt %	30	-
	Talc MP 10-52	WtPts	9.0	9.3
		Wt %	9.0	9.3
	Glass Fiber			20
	Izod Impact 23°C			
	Unnotched	(Ft Lbs/in)	27.5	31.2
15		(J/m)	1469	1666
	Izod Impact 23°C			
	Notched	(Ft Lbs/in)	0.8	0.9
		(J/m)	43	48
	Dart Impact			
	23°C	(In Lbs)	446	454
	-30°C	(In Lbs)	185	139
	Dart Impact**			
20	23°C	(In Lbs)	391	435
	-30°C	(In Lbs)	210	248
	Tens Strgth Yield	(psi)	10428	10631
		(MPa)	72	73
	Tensile Break	(psi)	7251	6887
		(MPa)	50	48
	% Elongation Break		30	48
25	Tensile Modulus	(psi x 1000)	550	579
		(MPa)	3792	3992
	Flex Modulus	(psi x 1000)	550	543
		(MPa)	3792	3744
	CLTE	x 10-5/°F	2.96	2.92
		x 10-5/°C	5.33	5.26

\*Not an example of the present invention.

\*\*Specimen thickness 0.10 inch (2.5 mm); impact velocity 16,000 inches/min (400 meters/min).

1. A filled polymer blend composition comprising (a) a carbonate polymer component; (b) a monovinylidene aromatic copolymer component not containing a grafted rubber polymer component; and (c) an inorganic filler which has a number average particle size less than or equal to 10 micrometers ( $\mu\text{m}$ ) and an average diameter to thickness ratio (D/T)  
5 of from 4 to 30.
2. A filled polymeric blend composition according to Claim 1 comprising (a) carbonate polymer in an amount of from 50 to 95 percent by weight based on weight of components (a) and (b); (b) monovinylidene aromatic copolymer in an amount of from 5 to 50 percent by weight based on weight of components (a) and (b); and (c) inorganic filler in an  
10 amount of from 1 to 17 percent by weight based on weight of components (a), (b) and (c).
3. A filled polymeric blend composition according to Claim 1 wherein the inorganic filler is selected from the group consisting of talc, clay and mixtures thereof.
4. A filled polymeric blend composition according to Claim 1 wherein the filler has an average diameter/thickness ratio of from 6 to 30.
5. A filled polymeric blend composition according to Claim 1 wherein at least  
15 99 percent of the filler has a particle diameter less than 44  $\mu\text{m}$ .
6. A filled polymeric blend composition according to Claim 1 wherein the inorganic filler is a hydrated magnesium silicate talc.
7. A filled polymeric blend composition according to Claim 1 wherein the  
20 inorganic filler has an average particle size of 2  $\mu\text{m}$  or below.
8. A filled polymeric blend composition according to Claim 1 wherein the inorganic filler has a maximum particle size of 30  $\mu\text{m}$  or below.
9. A filled polymeric blend composition according to Claim 1 wherein the carbonate polymer comprises in polymerized form one or more dihydroxy monomers selected  
25 from the group consisting of bisphenol A, tetrabromo-bisphenol A, tetramethyl bisphenol A, 1,1-bis(4-hydroxyphenyl)-1phenylethane, or bishydroxyphenylfluorene.
10. A filled polymeric blend composition according to Claim 1 wherein the carbonate polymer has a melt flow rate from 3 to 80 grams per 10 minutes.
11. A filled polymeric blend composition according to Claim 1 comprising a  
30 monovinylidene aromatic copolymer comprising copolymerized therein styrene and acrylonitrile.
12. A filled polymeric blend composition according to Claim 11 wherein the weight average molecular weight of the styrene and acrylonitrile copolymer is from 140,000 to 250,000.
13. A filled polymeric blend composition according to Claim 11 wherein  
35 the monovinylidene aromatic copolymer comprises from 15 to 35 percent by weight acrylonitrile based on weight styrene and acrylonitrile.

14. A filled polymeric blend composition according to Claim 1 wherein the carbonate polymer component comprises (a)(1) a rubber polymer impact modifier component.
15. A filled polymeric blend composition according to Claim 14 wherein the carbonate polymer component comprises (a)(1) a rubber polymer impact modifier component which is a grafted homopolymer or copolymer of butadiene which is grafted with a polymer of styrene and methyl methacrylate.
16. A filled polymeric blend composition according to Claim 15 wherein the monovinylidene aromatic copolymer comprises in polymerized form styrene and at least 23 weight percent acrylonitrile based on weight styrene and acrylonitrile.
17. A molded article prepared from a composition according to Claim 1 containing no rubber polymer impact modifier component.
18. A molded article prepared from a composition according to Claim 1.
19. A molded article according to Claim 18 which is an automobile interior instrument panel.
20. An improved process for reducing the die swell in processes for preparing extruded articles or pellets from carbonate polymer/monovinylidene aromatic copolymer blends comprising the step of extruding a polymer blend composition according to Claim 1 to form an article or a strand which is cut into pellets.

# INTERNATIONAL SEARCH REPORT

International Application No

PC1/US 95/09940

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L69/00 C08K3/34 C08K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 80-04425C(03) & JP,A,54 154 456 (HEXACHEMICAL KK) 5 February 1979 see abstract	1-11
Y	EP,A,0 391 413 (DOW CHEMICAL CO.) 10 October 1990 cited in the application see claims 1,4-8	1-11
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN JP60231763 & JP,A,60 231 763 (CALP. KOGYO KK) 18 November 1985 see abstract	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

30 November 1995

Date of mailing of the international search report

29.12.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (- 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (- 31-70) 340-3016

Authorized officer

O'Sullivan, T

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/09940

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Derwent Publications Ltd., London, GB; AN 86-016510(03) &amp; JP,A,60 238 332 (TOPPAN PRINTING KK) 27 November 1985 see abstract</p> <p style="text-align: center;">---</p>	1-20
A	<p>US,A,3 424 703 (JONES C.C.) 28 January 1969 cited in the application see claim 1</p> <p style="text-align: center;">-----</p>	1

Form PCT ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/09940

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0391413	10-10-90	US-A- 5091461	25-02-92
		AU-B- 630180	22-10-92
		AU-B- 5298690	11-10-90
		CA-A- 2014012	07-10-90
		JP-A- 2294358	05-12-90
		JP-B- 7033473	12-04-95
US-A-3424703	28-01-69	BE-A- 670376	17-01-66
		DE-B- 1285175	
		FR-A- 1456982	12-01-67
		GB-A- 1100175	
		NL-A- 6512670	04-04-66